

Thin-Film Photovoltaics Partnership Program

Report on Alternative Buffer Layer Technologies – Year II

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Project: **Fundamental Materials Research and Advanced Process Development for Thin-Film CIS-Based Photovoltaics**

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1 Development of Alternative Buffer Layers

1.1 Overview

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1.2 Objectives

The objective of this research task is to develop and optimize the chemical-bath-deposition (CBD) of CdS and Cd-free alternative buffer layers for the CIGS solar cells.

1.3 Introduction

The best performed CIGS solar cell was achieved by using CBD CdS buffer layers with a total area conversion efficiency of over 19% AM1.5G [1]. There are considerable interests in the study of alternative buffer layer materials such as (Cd,Zn)S [2,3], ZnS [2-4], $\text{Zn}_x(\text{O,S})_y$ [5], $\text{Zn}(\text{O,S,OH})_x$ [6], ZnO [7], $\text{Zn}(\text{O,OH})_x$ [7], $\text{In}_x(\text{OH,S})_y$ [2,3,8,9,10], In_2S_3 , $\text{In}(\text{OH})_3$, SnO_2 , $\text{Sn}(\text{S,O})_2$, ZnSe [7], $\text{Zn}(\text{Se,OH})_x$ [7], ZrO_2 , MnS [7], or $\text{Mn}(\text{S,OH})_x$ [7] deposited by CBD, ALE, MOCVD for CIGS solar cells. In addition, it has been reported that Cd-partial electrolyte treatment [11] modifies the CIGS surface favorably as evidence by the improvement in the performance of CIGS solar cells [12]. Using wider band-gap materials to replace the CdS ($E_g \approx 2.4\text{eV}$) buffer layer could improve the quantum efficiency of the CIGS cell at shorter wavelengths, resulting in an increase of short-circuit current. The (Cd,Zn)S buffer layer has a band-gap energy greater than 2.4 eV, and can provide a better lattice match to the CIGS absorber layer. The motivation for searching for alternative buffer layers over the CdS buffer layer is not only to eliminate toxic Cd but also to improve the light transmission in the short wavelength regime by using the wider band-gap materials. ZnS ($E_g \approx 3.6\text{eV}$) and $\text{In}(\text{OH})_x\text{S}_y$ ($E_g \approx 2.54\text{eV}$ [9]) buffer layers for CIGS solar cells have achieved high active-area conversion efficiencies of 16.9% [4] and 15.7% [10], respectively. The CIGS-based solar cells with a $\text{Zn}(\text{O,S})/\text{ZnO}$ bilayer buffer layer deposited by Atomic Layer Deposition (ALD) have reached a total area efficiency of 16.0% [13]. Thus, ZnS, $\text{In}(\text{OH})_x\text{S}_y$, $\text{Zn}(\text{O,S})$, and ZnO thin films are promising candidates for the Cd-free buffer layers for CIGS cells among the reported alternative materials.

1.4 Research Status of Alternative Buffer Layers

A study on the growth parameters of alternative buffer layers using (Cd,Zn)S, ZnS, and $\text{In}(\text{OH})_x\text{S}_y$ by chemical bath deposition (CBD) has been performed for the CIGS-based solar cells. Several CIGS cells with these buffer layers deposited by the optimal CBD process were fabricated. The performance of these CIGS cells were characterized by the J-V measurements and compared to the CIGS cells with CdS buffer layers. The recipe, chemicals, and deposition conditions of ZnO buffer layers are currently investigating. In addition, a new alternative buffer layer of $\text{Zn}_x(\text{O,S})_y$ using modified CBD is currently in progress. Furthermore, the effects of Cd-

partial-electrolyte treatments on the CIGS thin films were investigated and characterized by the Hall effect measurements.

The buffer layer materials of CdS, (Cd,Zn)S, ZnS, and $\text{In}(\text{OH})_x\text{S}_y$ were deposited on the soda-lime glass substrates, the $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGS), and the $\text{Cu}(\text{In,Ga})(\text{Se,S})_2$ (CIGSS) thin films by using CBD process. The impurities in the deposited films and their atomic concentration were characterized by the X-ray Photoelectron Spectroscopy (XPS) analysis. Both the CIGS and CIGSS samples deposited with the CdS, (Cd,Zn)S, ZnS, or $\text{In}(\text{OH})_x\text{S}_y$ buffer layers by the CBD process were fabricated into solar cells. The current-voltage (I-V) characteristics of these cells with the alternative buffer layers were measured, and the results were compared to the cells deposited with CBD CdS buffer layers. The results show comparable performance among these cells, and further optimization of the deposition conditions should improve the performance of the CIGS cells deposited with the alternative buffer layers.

1.5 The Chemical Bath Deposition (CBD) Conditions and Device Fabrication

The aqueous solution consisting of $2.4 \times 10^{-4}\text{M}$ CdCl_2 , $2.38 \times 10^{-3}\text{M}$ NH_2CSNH_2 , $7.43 \times 10^{-4}\text{M}$ NH_4Cl , and $6.61 \times 10^{-4}\text{M}$ NH_4OH at a bath temperature in the range of 80 to 85°C was applied to the deposition of CdS films. The CBD $\text{In}(\text{OH})_x\text{S}_y$ films were deposited using a freshly prepared aqueous solution of 0.005M indium chloride and 0.15M thioacetamide at 70°C with deposition times varied between 15 and 25 minutes and with a pH value of 1.8. In order to avoid nucleation centers in the bath for the deposition of $\text{In}(\text{OH})_x\text{S}_y$, the insoluble particles present in the stock solution of thioacetamide were eliminated by filtration. The complexing agent, acetic acid, was added into the bath during the deposition of $\text{In}(\text{OH})_x\text{S}_y$ as a new deposition condition to improve the film quality. The deposition of (Cd,Zn)S buffer layers was carried out with $1.2 \times 10^{-3}\text{M}$ CdCl_2 , $6.27 \times 10^{-4}\text{M}$ ZnCl_2 , $1.2 \times 10^{-2}\text{M}$ thiourea, $5.27 \times 10^{-4}\text{M}$ NH_3 , and $1.39 \times 10^{-3}\text{M}$ NH_4Cl , and the bath temperature was maintained at around 85°C. For the CBD ZnS films the deposition bath was prepared with an aqueous solution of $2.5 \times 10^{-2}\text{M}$ ZnSO_4 , $3.5 \times 10^{-2}\text{M}$ thiourea, 1M NH_3 , and 3M hydrazine at a bath temperature varied between 70 and 80°C.

The CdS, (Cd,Zn)S, ZnS, or $\text{In}(\text{OH})_x\text{S}_y$ buffer layers were deposited on the CIGS and CIGSS samples provided by Institute of Energy Conversion (IEC) of the University of Delaware, ISET, or Siemens Solar Industries. The high/low resistivity ZnO bilayer films were then deposited by either MOCVD or sputtering technique on these samples. Ni/Al grids as contact pads were finally deposited to obtain the finished cells.

1.6 Compositional Analysis of CdS, (Cd,Zn)S, ZnS, and $\text{In}(\text{OH})_x\text{S}_y$ Buffer Layers

The near surface composition of the CdS, (Cd,Zn)S, ZnS, and $\text{In}(\text{OH})_x\text{S}_y$ films deposited on the soda-lime glass substrates or CIGS samples were characterized by the X-ray Photoelectron Spectroscopy (XPS), and the results are shown in Figure 1.1. The XPS analysis was conducted by using a Physical Electronics 5100 ESCA equipped with a Mg $\text{K}\alpha$ X-ray source and a hemispherical analyzer. Depth profiling was performed with an argon ion source operating at the beam energy of 4 KeV. The charging effects were taken into account by

referring the measured spectra to the binding energy peak of C 1s at 285 eV. Carbon was initially present for all films deposited by the CBD process but became undetectable during sputter depth profiling, indicating that little carbon was incorporated in the films. Besides carbon elements of metal (Cd, Zn, or In), sulfur, and oxygen were also identified in the deposited films.

Before and after sputtering the CBD CdS films the binding energy peaks of Cd 3d_{5/2} and S 2p_{3/2} at about 405.3eV and 161.5eV were obtained, respectively. The result shows that the sulfur peak is in good agreement with the reported data (S-Cd: 161.7eV [14]). The binding energies of Cd-S (405.3eV [14]), Cd-O (405.2eV [14]), and Cd-OH (405.0eV [14]) are too close to identify the exact compounds presented in the film from the measured Cd peak at 405.3eV. Two peaks at 529.48eV and 531.09eV obtained from the deconvolution of O 1s binding energy curve demonstrate that the film consists of chemical bonds Cd-O (529.2eV [14]) and Cd-OH (530.9-532eV [14]). The estimated atomic concentration ratios of [Cd]/[S] and [S]/[O] are approximately 1.6 and 5.4, respectively. For the (Cd,Zn)S film the atomic concentration was estimated from the peak area of each element, Cd, Zn, S, and O, in the film. The XPS result indicated that a large amount of oxygen (around 40%) and a small amount of zinc (around 2%) were incorporated in the (Cd,Zn)S film. Because the precipitation of CdS is easier and faster than that of ZnS during the CBD process, the deposited (Cd,Zn)S film only had a very small quantity of zinc even though the concentration of zinc source was an order of magnitude higher than that of cadmium source in the deposition bath.

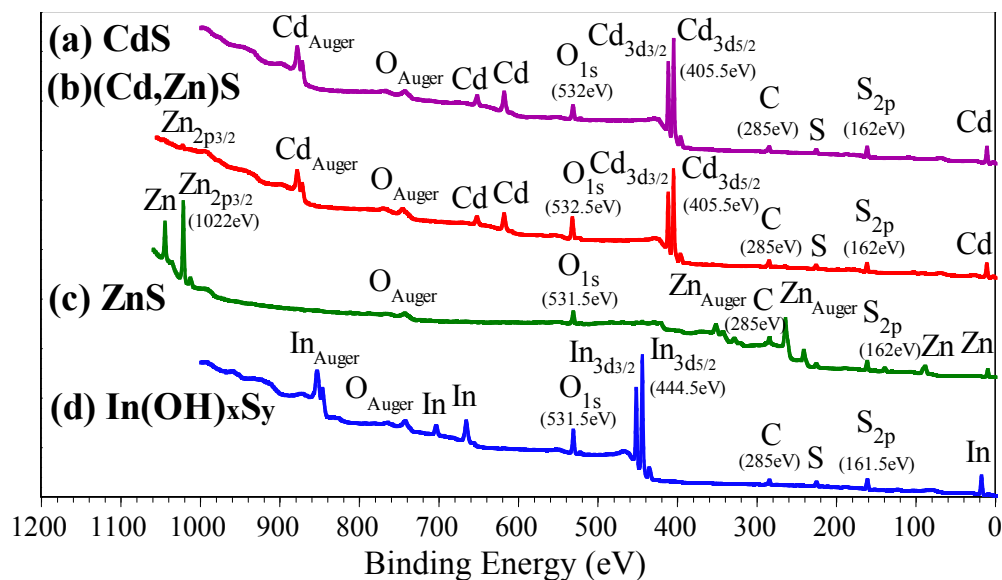


Figure 1.1 XPS spectra of CdS, (Cd,Zn)S, ZnS, or In(OH)_xS_y thin films deposited on CIGS thin films by the CBD process.

For the ZnS film, the deconvolution of Zn 2p_{3/2} binding-energy spectrum from 1018eV to 1026eV revealed only one peak at 1022.0eV. This is consistent with the energy peaks of possible compounds ZnS and/or ZnO at 1022.0eV and 1021.8eV-1022.5eV [14], respectively. No evidence of ZnSO₄ was found from the Zn 2p_{3/2} peak, where the binding energy peak of ZnSO₄ is 1023.1eV. The oxygen 1s photoelectron binding energy spectra were fitted with Gaussian-Lorentzian curves both before and after sputtering the film. The XPS spectra can be

represented by two peaks at about 530.6-530.1eV and 531.6eV, which correspond to the chemical bonds of Zn-O (530.4eV [14]) and metal-hydroxide compound (530.9-532eV [14]), respectively. Thus the results suggest that the CBD ZnS films might be a mixture of ZnS, ZnO, and Zn(OH)₂. The estimated atomic concentration ratio of Zn, S, and O was about 5:3:2 after sputtering the film for 4 minutes. For the In(OH)_xS_y films deposited by CBD with acetic acid in the bath, a binding energy peak of S 2p_{3/2} was found at about 161.24eV, which can be assigned to the sulfide compound.

1.7 J-V Characterization of CIGS-based Solar Cells with CdS, (Cd,Zn)S, ZnS, or In(OH)_xS_y Buffer Layers and Progress on Zn_x(O,S)_y or ZnO Buffer Layers

1.7.1 The CIGS-based Cells with CdS or (Cd,Zn)S Buffer Layers

The J-V characteristics of CIGSS solar cells with CdS or (Cd,Zn)S buffer layers deposited by our baseline CBD process are shown in Figure 1.2, where the CIGSS absorbers are provided by Siemens Solar Industries. Evidently the CIGSS solar cell with CdS buffer layer has the best conversion efficiency. On the contrary the performance of the other cells deposited with (Cd,Zn)S, ZnS, or In(OH)_xS_y buffer layers has a lower conversion efficiency than that of the CdS/CIGSS cell. From the results of this study further optimization of the alternative buffer layers is needed, which includes the optimization of the deposition conditions to improve the film quality and the investigation of the effects of post-deposition annealing and light soaking on the devices.

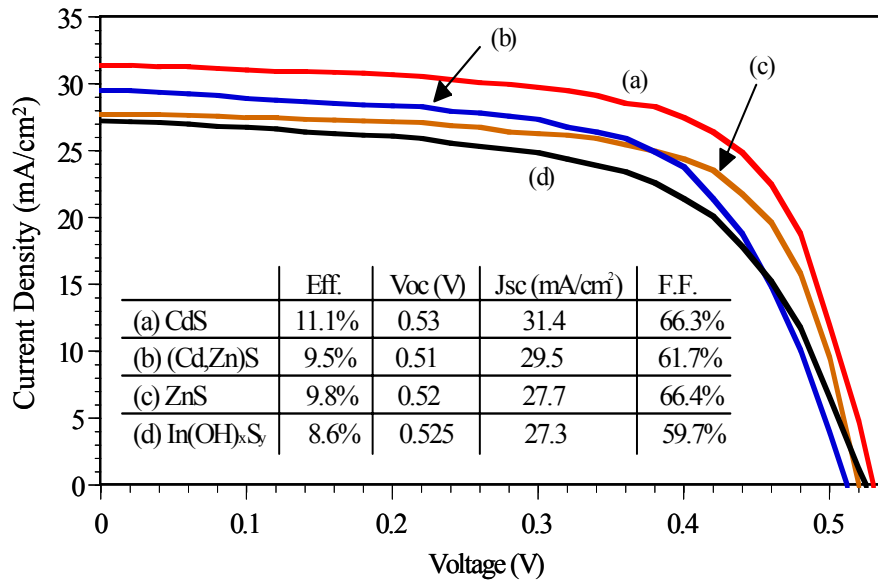


Figure 1.2 The J-V characteristics of the CIGSS cells with CdS, (Cd,Zn)S, ZnS, or In(OH)_xS_y buffer layers.

1.7.2 The CIGS-based Cells with ZnS Buffer Layers

Figure 1.3 illustrates the effect of ZnS buffer layer thickness on the performance of the Siemens CIGSS solar cells. With the increase of the ZnS buffer layer thickness the absorption of incident light in the ZnS layer increases, and thus the short-circuit current of the cell decreases. Due to the high resistivity of the ZnS buffer layer a thick buffer layer can cause a high series resistance in the solar cell and results in poor fill factor as shown in Figure 1.3. With the higher band gap of ZnS than that of CdS, the ZnS/CIGSS cell should have a higher short-circuit current than the CdS/CIGSS cell because of the higher quantum efficiency at the shorter wavelength region. However, the highest short-circuit current obtained in this study for the ZnS/CIGSS cell was only 27.7 mA/cm² (see Figure 1.2), whereas for the CdS/CIGSS cell a short-circuit current of 31.4 mA/cm² was obtained. Thus, further optimization of ZnS layer thickness and deposition condition is needed in order to achieve the potential of ZnS buffer layers for CIS-based cells.

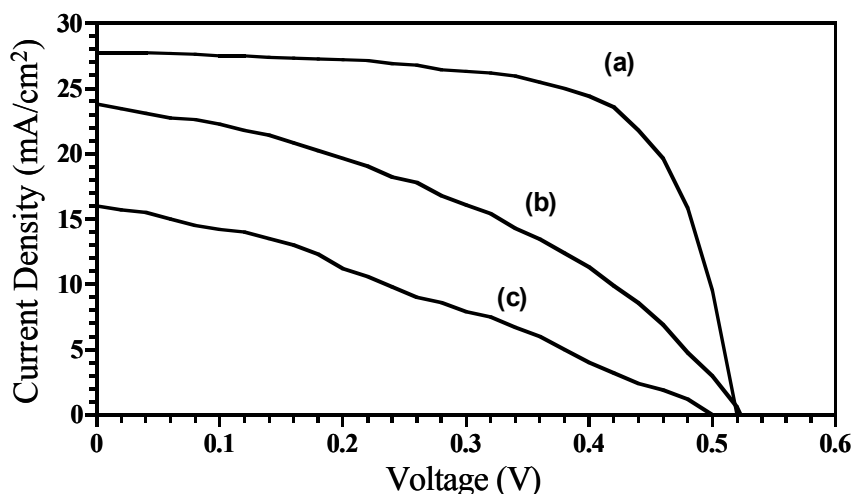


Figure 1.3 The J-V characteristics of CIGSS solar cells using different thickness of CBD ZnS buffer layers deposited for (a) 10min, (b) 20min, and (c) 25min at 70°C.

1.8 CIGS-based Cells with In(OH)_xS_y Buffer Layers

Each I-V measurement for the CIGS cells comprised a sweep in the I_{SC} to V_{OC} direction followed immediately by a sweep from V_{OC} to I_{SC} direction. The dark- and photo- I-V curves of the In(OH)_xS_y/CIGS heterojunction cell before and after annealing at 200°C in the air for 20 minutes are shown in Figure 1.4. As illustrated a hysteresis loop was observed in the photo- I-V curves of the In(OH)_xS_y/CIGS cells before and after annealing. On the contrary, no evidence of a hysteresis loop in the photo-I-V curves of the CdS/CIGS cells was found in this study.

Initially the device without annealing showed the inflected I-V curve. The fill factor (F.F.),

J_{SC} , V_{OC} , and hence conversion efficiency were dramatically improved after annealing time of 20 minutes. The cells, however, showed the degradation when the total annealing time was increased to 40 minutes. In order to improve the cell performance, it is necessary to optimize the annealing conditions.

Comparing the performance of CdS/CIGS cells and $\text{In}(\text{OH})_x\text{S}_y/\text{CIGS}$ cells, we have found that the latter has a much higher open-circuit voltage, a comparable short-circuit current density, and a very poor fill factor ($V_{OC} = 0.57\text{V}$, $J_{SC} = 29.1\text{mA}/\text{cm}^2$, F.F. = 44.6%, and conversion efficiency $\eta = 7.39\%$) as shown in Figure 1.5, while the CdS/CIGS cell yields a conversion efficiency of 9.99%, $V_{OC} = 0.51\text{V}$, $J_{SC} = 30.5\text{mA}/\text{cm}^2$, and F.F. = 63.8%. The possible reason why the $\text{In}(\text{OH})_x\text{S}_y/\text{CIGS}$ cell has a higher V_{OC} is that the net acceptor concentration in the CIGS layer is increased and hence the depletion width is reduced. The CBD alternative buffer layer process might influence the charged states at the surface or at the grain boundaries of the CIGS layer and hence modify the electrical properties of the absorber layer as well [10]. However, the $\text{In}(\text{OH})_x\text{S}_y/\text{CIGS}$ cell has a lower J_{SC} due to the lower quantum efficiency than the CdS/CIGS cell in the long wavelength region [10]. By adding the complexing agent of acetic acid into the chemical bath, a more adherent, reproducible, homogeneous, and higher quality $\text{In}(\text{OH})_x\text{S}_y$ film [15] has been deposited on the glass substrates and on Siemens CIGSS samples. The performance of one CIGSS cell deposited with $\text{In}(\text{OH})_x\text{S}_y$ buffer layer using acetic acid and the comparable performance of the CIGSS cells deposited with the other buffer layers are shown in Figure 1.2. The result reveals that we can take advantage of the $\text{In}(\text{OH})_x\text{S}_y$ buffer layer deposited by the new deposition method to improve the device performance.

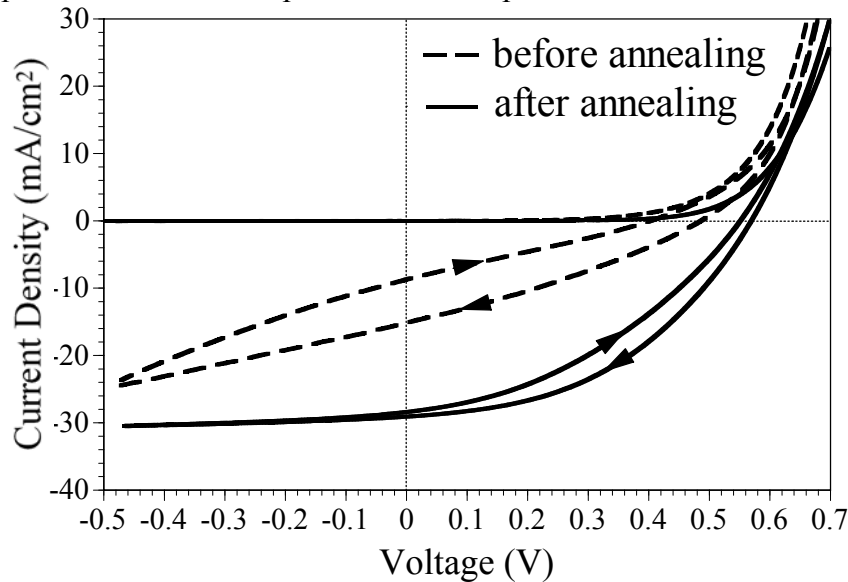


Figure 1.4 The J-V characteristics of the CIGS cell deposited with CBD $\text{In}(\text{OH})_x\text{S}_y$ buffer layer before and after annealing.

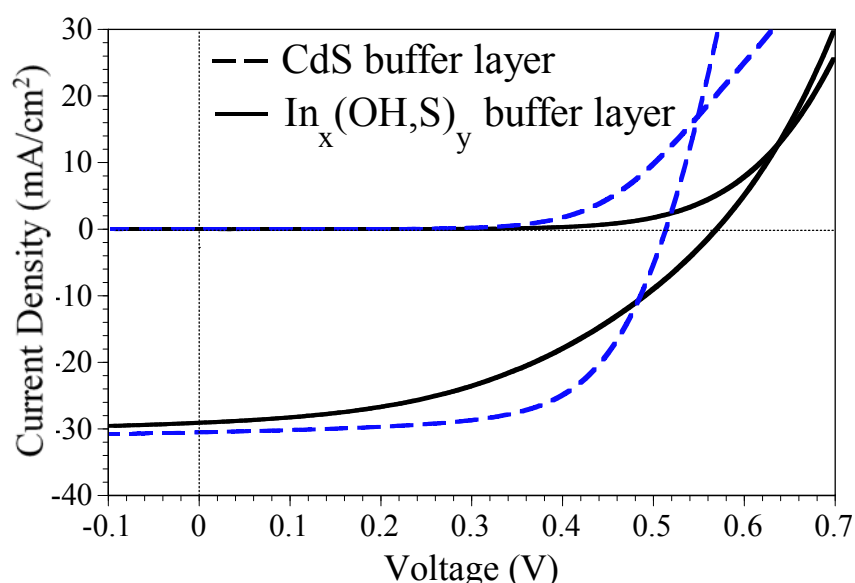


Figure 1.5 The J-V characteristics of the CIGS cells with CBD- CdS or CBD- $\text{In}_x(\text{OH},\text{S})_y$ buffer layer (CdS/CIGS solar cell: Eff.=9.99%, V_{oc} =0.51V, J_{sc} =30.5mA/cm², F.F.=63.8%; $\text{In}(\text{OH})_x\text{S}_y$ /CIGS solar cell: Eff.=7.39%, V_{oc} =0.57V, J_{sc} =29.1mA/cm², F.F.=44.6%).

1.8.1 Recent Progress on CBD $\text{Zn}_x(\text{O},\text{S})_y$ and ZnO Buffer Layers

The aqueous solutions of 0.1 M ZnSO_4 mixed with 5.0 M NH_3 and 0.1 M Na_2S at room temperature bath have been applied for the deposition of $\text{Zn}_x(\text{O},\text{S})_y$ thin films using modified chemical bath deposition process [5]. The glass substrate was immersed in ZnSO_4 solution to absorb Zn^{2+} and OH^- ions on the surface of the substrate. The substrate was rinsed in the deionized (DI) water. The glass substrate was then immersed in Na_2S solution to absorb S^{2-} ions and react with Zn^{2+} ions, and was rinsed in the DI water to remove loosely bounded particles and unreacted ions. Such deposition steps are repeated to obtain a desired $\text{Zn}_x(\text{O},\text{S})_y$ film thickness. The chemical preparation and deposition conditions of $\text{Zn}_x(\text{O},\text{S})_y$ buffer layers are investigated. The progress of this buffer layer deposition and characterization will be reported next quarters with their structural, compositional, optical, and electrical properties, and device fabrication of the CIGS-based solar cells with $\text{Zn}_x(\text{O},\text{S})_y$ buffer layers will also be carried out. Furthermore, ZnO buffer layer, another candidate of alternative buffer layers, will be investigated, and the results of the J-V measurements on the ZnO deposited CIGS cells will be compared with the CIGS cells deposited with CdS buffer layers.

1.9 Investigation of the Effect of Cd-partial-electrolyte Treatments on CIGS Films

Similar to the procedure for the deposition of CdS buffer layer by using CBD, the aqueous solution consisting of $2.4 \times 10^{-4}\text{M}$ CdCl_2 , $7.43 \times 10^{-4}\text{M}$ NH_4Cl , $6.61 \times 10^{-4}\text{M}$ NH_4OH at a bath temperature in the range of 80 to 85°C was applied to the Cd partial-electrolyte treatments. In order to remove the possible precipitation, which may be deposited on the surface of the films, the samples were thoroughly rinsed with DI water after the deposition and blown dry with

nitrogen stream.

Four 1×1 inch identical CIGS samples which were cut from a 2×2 inch uniform slab were applied by Cd-partial-electrolyte treatment with different soaking times. Hall measurements were made to characterize the effect of Cd-partial-electrolyte treatments on the carrier density and mobility of the samples, and the results are summarized in Table 1-1. The results reveal that Cd-partial-electrolyte treatments increase hole density and decrease Hall mobility with increasing Cd-treatment time. No correlation was found between the resistivity and the Cd-dip time. One possible explanation of this effect is that during the Cd-partial-electrolyte treatment, Cd ions occupy the Cu- vacancy sites and create donors with densities in the range of 10^{17} - 10^{18}cm^{-3} , thus an ultra-thin n- type surface inversion layer (5-10 nm) is formed [16]. The mixed conduction of electrons in such layer and holes in the p-CIGS absorber layer decreases the measured Hall coefficient and consequently yields higher hole density in the Cd-dip CIGS films.

Table 1.1 Hall measurement results for the different Cd-partial-electrolyte treatment times on the CIGS samples. (Note: the carrier conduction types for all CIGS samples tested are p-type assuming a uniform sample.)

samples	Hole density (cm^{-3})	Hall mobility ($\text{cm}^2/\text{V}\cdot\text{s}$)	Resistivity ($\Omega\cdot\text{cm}$)
1. No treatments	5.3×10^{15}	8.89	133
2. Cd-dip (15 mins)	2.9×10^{16}	0.93	235
3. Cd-dip (15 mins)	4.3×10^{16}	1.54	94
4. Cd-dip (30 mins)	7.1×10^{16}	0.60	148

1.10 Summary and Conclusions

A study of the electrical and optical properties of CBD buffer layers on soda-lime glass substrates and on absorber layers was conducted. The XPS results indicated that CdS, (Cd,Zn)S, ZnS, and $\text{In}(\text{OH})_x\text{S}_y$ films deposited by the CBD method were not completely pure. A small amount of carbon was found to incorporate in the first few atomic layers of the films. Also oxygen in the form of metal oxide and/or metal hydroxide was incorporated into the films during the deposition process. A better quality $\text{In}(\text{OH})_x\text{S}_y$ buffer layer has been achieved by adding the acetic acid into the reaction bath. Annealing has been found to be a key factor for improving the conversion efficiency of CIS-based cells deposited with alternative buffer layers. Among the CIS-based solar cells with CdS, (Cd,Zn)S, ZnS, or $\text{In}(\text{OH})_x\text{S}_y$ buffer layers studied in this work, the CdS/CIGSS cell gives the best performance [2,3,8,9]. The Cd-partial-electrolyte treatments on the CIGS cells increased hole density and decreased Hall mobility with increasing Cd treatment time.

1.11 Future Work

Our efforts for the CIGS-based solar cells with alternative buffer layers of (Cd,Zn)S, ZnS,

and $\text{In}(\text{OH})_x\text{S}_y$ will focus on optimizing the annealing and CBD process conditions. For buffer layers of ZnO and $\text{Zn}_x(\text{O},\text{S})_y$, recipes will be developed for the fabrication of CIGS cells. Furthermore, the buffer layers of CdS and $(\text{Cd},\text{Zn})\text{S}$ will be deposited on the wide band gap CGS cells to compare the performance of CGS solar cells deposited with these buffer layers. To achieve uniform surface of buffer layers, Atomic Layer Deposition (ALD) will be investigated and compared to the buffer layers by the CBD process.

1.12 Publications and Conference Presentations

1. C.H. Huang, Sheng S. Li, L. Rieth, A. Halani, M.L. Fisher, Jiyon Song, T.J. Anderson, and P.H. Hoplloway, "A comparative study of Chemical-Bath-Deposited CdS, $(\text{Cd},\text{Zn})\text{S}$, ZnS, and $\text{In}(\text{OH})_x\text{S}_y$ buffer layers for CIS-based solar cells," *Conf. Record of the 28th IEEE Photovoltaic Specialists Conference*, pp. 696-699 (2000).
2. C.H. Huang, Sheng S. Li, L. Rieth, A. Halani, Jiyon Song, T.J. Anderson, and P.H. Holloway, "A comparative study of Chemical-Bath-Deposited CdS, $(\text{Cd},\text{Zn})\text{S}$, ZnS, and $\text{In}(\text{OH})_x\text{S}_y$ buffer layers for CIS-based solar cells," *Proceedings of the 2000 NCPV (National Center for Photovoltaics) Program Review Meeting*, Denver, Colorado, pp. 229-230 (2000).
3. C.H. Huang, Sheng S. Li, W.N. Shafarman, C.-H Chang, E.S. Lambers, L. Reith, J.W. Johnson, S. Kim, B.J. Stanbery, T.J. Anderson, and P.H. Holloway, "Study of Cd-free Buffer Layers Using $\text{In}_x(\text{OH},\text{S})_y$ on CIGS Solar Cells," *Solar Energy Materials and Solar Cells*, vol. 69, pp. 131-137 (2001).
4. C.H. Huang, Sheng S. Li, W.N. Shafarman, C.-H Chang, J.W. Johnson, L. Reith, S. Kim, B.J. Stanbery, and T.J. Anderson, "Study of Cd-free Buffer Layers Using $\text{In}_x(\text{OH},\text{S})_y$ on CIGS Solar Cells," *Technical Digest of the 11th International Photovoltaic Science and Engineering Conference*, Hokkaido, Japan, September 20-24, pp. 855-856 (1999).

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(National Center for Photovoltaics) Program Review Meeting, Denver, Colorado, pp. 229-230 (2000).

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